

## POLYMERIC SURFACTANTS PREPARED BY TRANSESTERIFICATION OF HYDROXYETHYLCELLULOSE WITH METHYL ESTER OF RAPE SEED OIL AND TRIACYL GLYCERIDES

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**ABSTRACT:** Polymeric surfactants were prepared from O - (2 - hydroxyethyl) cellulose (HEC, DS = 1) by transesterification with methyl esters of rape seed oil (MERO) with or without K<sub>2</sub>CO<sub>3</sub> as catalyst and triacyl glycerides (rape seed oil) using potassium laurate as catalyst in system H<sub>2</sub>O/DMF under the influence of microwave energy. The various reaction conditions were used to optimize the preparation of water – soluble esters. Synthesis under microwave heating were realized analogical as described by the preparation of cellulose stearate [1]. The obtained esters of hydroxyethylcellulose were characterized by FTIR spectral data. The surface – active and performance properties were determined (surface tension of water, emulsifying efficiency, foamability, washing performance, antiredeposition efficiency). The results suggested that the partially hydrophobized HEC esters are potential biosurfactants, which might be exploited in various technical applications. Application of microwave energy might contribute to a more economic process due to substantial shortening of reaction time.

**KEY WORDS:** hydroxyethylcellulose, transesterification, microwave irradiation, Methyl ester of rape seed oil, Triacyl glycerides, polymeric surfactants

### 1. INTRODUCTION

During the last years, many research activities have been focused on hydrophobically modified polysaccharides because of the interesting functional properties of these derivatives, which provide uses as surfactants, associative thickeners, etc. over a wide field of application. Various commercial and non – commercial polysaccharides, such as alginate [2, 3], chitosan [4,5], pectin [6], hydroxyethylcellulose [7-9], carboxymethylcellulose [10], carboxymethyl starch [11,12], glucuronoxylan [13,14] have been used to prepare polymeric surfactants. O – (2 – Hydroxyethyl) cellulose (HEC) is water – soluble, nonionic ether, which represents a potencial source of biopolymers for further chemical modification. Recently, some alternative esterification methods, such as esterification with mixed anhydrides prepared „in situ“ [15] transesterification with vinyl carboxylic acid esters like vinyl laurate [16] and transesterification with fatty acid methyl esters [17] have been developed to avoid the use of acid halides. Partial hydrophobization of HEC using mixed anhydrides and vinyl laurate [9] was performed under relatively mild reaction conditions (low reactant to HEC weight ratios, low temperature and/or short reaction time). In contrast to cellulose, no special solvent systems or pretreatments were necessary owing to the solubility of HEC in aprotic solvents, which is an important advantage of these hydrophobization techniques. In spite of the very low degrees of

substitution achieved, the new synthesized HEC derivatives exhibited very positive surface – active and performance properties [9].

Microwave irradiation is becoming an increasingly popular method of heating which replace the classical one because it proves to be a clean, cheap and convenient method. Often, it affords higher yields and results in shorter reaction times. The efficiency of microwave heating is in the dramatical reduction reaction times (from days and hours to minutes and seconds) is just one of the many advantages of methods performed under microwave irradiation. Microwave techniques find application in many diverse areas of chemistry, including analytical chemistry, organic and inorganic synthesis, manufactures of ceramics, pharmaceutical chemistry and catalysis [18]. Recently, the method of microwave heating has been used for microwave – assisted cellulose acylation in homogeneous phase [19], transesterification of methylstearate with low – molecular microcrystalline cellulose under microwave heating [1], esterification of cellulose with long chain acyl chloride in homogeneous media [20], utilization of microwave irradiation for transesterification of carboxymethylcellulose [21], preparation of biodegradable plastic in microwave oven and „solvent – free“ conditions [22]. The present work is concerned to transesterification of HEC with the methyl ester of rape seed oil (MERO) in system  $H_2O/DMF$  with and without  $K_2CO_3$  as catalyst and the triacyl glycerides (rape seed oil) in system  $H_2O/DMF$  using potassium laurate as catalyst which was used analogical as described in [23] under the microwave irradiation. Various reaction conditions were used to optimize the preparation of water – soluble partially hydrophobized esters of HEC with emulsifying and detergent properties.

## 2. EXPERIMENTAL

### 2.1 Materials and analytical methods

The water - soluble HEC, Tylose H 4000/P2, ( $MS = 2.5$  and  $DS = 1$ ) was from Hoechst (Frankfurt am Main, Germany). The calculated molecular mass of the repeating unit of HEC was 271.  $N, N$  – Dimethylformamide (DMF), acetone and  $K_2CO_3$  were purchased from Lachema (Brno, Czech Republic). The methyl ester of rape seed oil (MERO) was obtained from VÚTCH – Chemitex, s.r.o. (Žilina, Slovakia) and contains oleic acid (58 %), linoleyl acid (17 %), linolenyl acid (17 %) and saturated  $C_{14} - 20$  fatty acids (8 %). The rape seed oil was commercial product from PALMA – TUMYS a. s. (Bratislava, Slovakia). The potassium laurate was prepared from lauric acid and potassium hydroxide (molar ratio, 1 : 1). Sodium dodecyl sulfate (SDS) and Tween 20 (oxyethylated sorbitol monolaurate) were commercial products from Sigma - Aldrich Chemie (Steinheim, Germany).

Esterification methods has been carried out in domestic microwave reactor „SENCOR“ by applying 1000 W power (DAEWOO ELECTRONICS). The HEC esters were characterized by FTIR spectroscopy, measured in KBr pellets using the NICOLET Magna 750 spectrometer with DTGS detector and OMNIC 3.2 software using 128 scans at a resolution of  $4\text{ cm}^{-1}$ . The samples (2 mg) were pressed into pellets of KBr (200mg).

### 2.2 Transesterification of hydroxyethylcellulose with the methyl ester of rape seed oil (MERO) and the triacyl glycerides (rape seed oil)

HEC (1.6 g) was dissolved in distilled water (10 ml) and stirred at room temperature for 0.5 - 1h. Subsequently to this solution was added the MERO or rape seed oil (1.6 g, for mass ratio HEC : MERO 1 : 1), dispersed in DMF (5 ml) and potassium laurate dissolved in distilled water (1 ml) was used as catalyst by transesterification HEC with rape seed oil. The prepared reaction mixture was homogenized at 30 500 rpm for 30 s in the case when MERO was used. The reaction mixture with rape seed oil was prepared without homogenization. The homogeneous reaction mixture was exposed

to microwave heating for 1 – 2 min with power of 660 W. The reaction product was subsequently precipitated into a volume of acetone that was 5 times larger than the reaction mixture, after 24 h was product separated by vacuum filtration over fritted glass, thoroughly washed with acetone and then purified by Soxhlet extraction with acetone for 8 h. In some experiments, the product was dissolved in distilled water and purified by dialysation and lyophilization. Reaction conditions and yields of water – soluble HEC esters are given in Table 1.

**Tab.1:** Reaction conditions and yields of water – soluble HEC derivatives obtained by transesterification with MERO and rape seed oil in H<sub>2</sub>O/DMF with controlled power of 660 W.

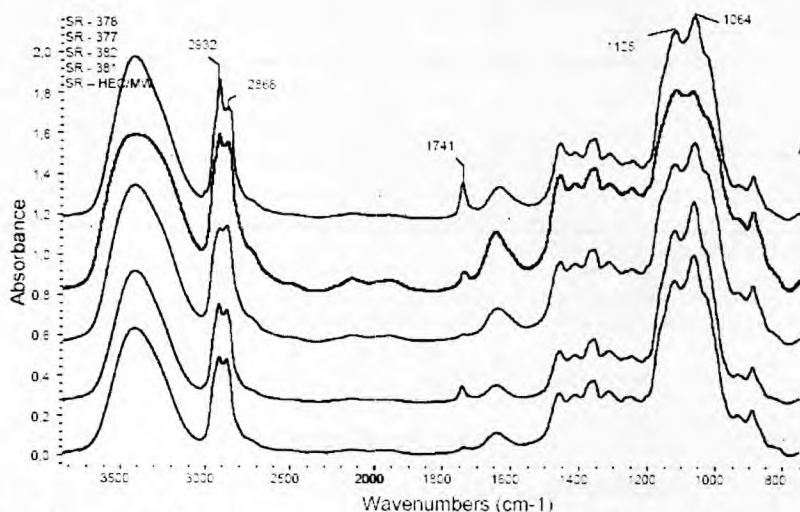
Derivative	SR	Mass ratio HEC : MERO	Time (min)	Temperature (°C)	Yield* (g/g)
HEC/1	SR - 355	1 : 1	1	92	0.72
HEC/2	SR - 337	2 : 1	1	93	0.69
HEC/3	SR - 357	3 : 1	1	96	0.71
HEC/4	SR - 347	4 : 1	1	88	1.05
HEC/5	SR - 338	1 : 1	2	96	1.06
HEC/6	SR - 338/6	1 : 2	2	90	1.00
HEC/7 <sup>a)</sup>	SR - 372	1 : 2	1	100	0.95
HEC/8 <sup>a) b)</sup>	SR - 373	1 : 1	2	90	1.05
		<b>HEC : rape seed oil</b>			
HEC/9 <sup>c)</sup>	SR - 377	1 : 1	5	177	0.86
HEC/10	SR - 378	1 : 1	2	90	0.86
HEC/11 <sup>d)</sup>	SR - 382	1 : 1	2	90	0.73
HEC/12	SR - 380	1 : 2	2	91	0.75
HEC/13	SR - 381	2 : 1	2	85	0.81

\* expressed as g of the recovered derivative per g HEC

- a) reaction time was measured after 5 minutes and derivatives were exposed the controlled power of 250 W in microwave reactor "MILESTONE"
- b) K<sub>2</sub>CO<sub>3</sub> was used as catalyst [24]
- c) derivative was prepared using „solvent - free“ technique by classical heating
- d) derivative was prepared without solvent DMF under microwave irradiation

### 2.3 Characterization of the obtained HEC esters

The prepared products were characterized by FTIR spectroscopy. The FTIR spectra of the derivatives show absorption bands or shoulders for ester groups at ~ 1741 cm<sup>-1</sup>. The  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  vibrations of the fatty acid substituents are present at ~ 2932 cm<sup>-1</sup> and ~ 2868 cm<sup>-1</sup>.



**Fig. 1:** FTIR spectra (in KBr) of the prepared HEC esters by transesterification with rape seed oil

## 2.4 Testing methods

### Surface – active properties of HEC derivatives

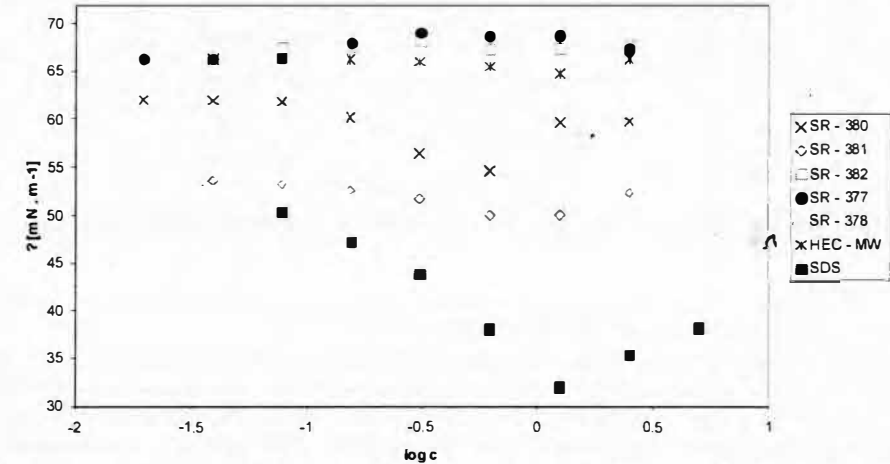
All products were characterized by emulsifying efficiency. The emulsifying efficiency was tested on oil – in – water (O/W) type emulsion prepared by mixing water (9 ml), containing of the tested HEC derivative (0.05 g) and paraffinic oil (1 ml) dyed with Sudan IV in the laboratory minimixer (Heindolph DIAX 900) at 30 500 rpm for 1 min. The stability of the emulsion was estimated at three different time intervals after the emulsions had been prepared, i. e. 5 min ( $h_1$ ), 1 h ( $h_2$ ) and 24 h ( $h_3$ ), and expressed in terms of the height of the oil (mm) and cream layers (mm) formed on the surface of the emulsion. The surface tension of aqueous polysaccharide solutions of the some tested derivatives in the concentration range  $0.0012 - 5 \text{ kg.m}^{-3}$  was determined at laboratory temperature using the Du Nouy ring method [25]. The surface tension data were plotted against HEC esters concentration in order to obtain the critical micelle concentration (c.m.c) and the corresponding minimum surface tension ( $\gamma_{\min}$ ). The results are given in Table 2.

**Tab.2:** Surface – active properties (surface tension,  $\gamma_{\min}$ , critical micelle concentration, c.m.c., and emulsifying efficiency) HEC derivatives and controls

Derivative	SR	$\gamma_{\min}$ (mN.m <sup>-1</sup> )	c.m.c (kg.m <sup>-3</sup> )	oil layer/cream layer* (mm/mm)		
				$h_1$	$h_2$	$h_3$
HEC/1	SR - 355	-	-	0/0	0/0	0/5.5
HEC/2	SR - 337	60.22	0.125	0/0	0/0	0/13
HEC/3	SR - 357	58.80	0.313	0/0	0/0	0/4
HEC/4	SR - 347	-	-	0/0	0/0	0/3
HEC/5	SR - 338	49.76	0.031	0/0	0/0	0/8
HEC/6	SR - 338/6	42.80	2.500	0/0	0/0	0/12
HEC/7 <sup>a.)</sup>	SR - 372	50.91	1.250	0/0	0/0	0/12
HEC/8 <sup>a.) b.)</sup>	SR - 373	57.83	-	0/0	0/0	0/4
HEC/9 <sup>c.)</sup>	SR - 377	66.46	-	0/0	0/0	0/10
HEC/10	SR - 378	50.95	-	0/0	0/0	0/10
HEC/11 <sup>d.)</sup>	SR - 382	66.68	0.039	0/0	0/0	0/10

HEC/12	SR - 380	54.67	0.625	0/0	0/0	0/10
HEC/13	SR - 381	49.96	0.625	0/0	0/0	0/3
Tween 20		-	-	0/0	0/0	0/11
Water		72.80	-	-	-	-
HEC		61.70	1.250	0/0	0/0	0/6
HEC/MW		64.80	1.250	0/0	0/0	0/5
SDS		32.00	1.250	-	-	-

SDS – Sodium dodecyl sulphate  
(-) – not determined



**Fig. 2:** Surface tension versus logarithm of polymer concentration (\* – height of oil and cream layers formed on the surface of the emulsion after 5 min (h<sub>1</sub>), 1 h (h<sub>2</sub>) and 24 h (h<sub>3</sub>))

### Performance testing methods

The washing power (WP) and antiredeposition efficiency (ARE) some of the tested derivatives at concentration 0.5 kg.m<sup>-3</sup> (WP) and 5 kg.m<sup>-3</sup> (ARE) were determined by the methods described in more detail in a previous paper [9] using a model soil and cotton fabric (SK – standard 800 101). WP was assessed by determining the reflectance of an artificially soiled cotton fabric after washing in an alkaline surfactant bath. The washing time for WP was 10 min, for ARE 60 min and the washing temperature for WP was 50 °C, 80 °C and for ARE 60 °C. The foamability (F) of aqueous solutions of the prepared HEC esters at concentration 1 kg.m<sup>-3</sup> was determined at laboratory temperature using the method described in a previous paper [26].

**Tab. 3:** Washing power (WP), antiredepositive efficiency (ARE) and foamability (F) of HEC esters and controls

Derivative	WP <sub>80°C</sub> (%)	WP <sub>50°C</sub> (%)	ARE <sub>60°C</sub> (%)	F (%)
HEC/1	-	-	-	78.6
HEC/2	95.0	-	84.7	80.7
HEC/3	-	-	-	73.1
HEC/4	96.0	-	50,1	65,9
HEC/5	96.2	-	86,3	32.1
HEC/6	-	86,3	-	32.1
HEC/7 <sup>a.)</sup>	-	82,0	80,5	20.7
HEC/8 <sup>a.)b.)</sup>	-	82,2	86,0	75.9



HEC/9 <sup>c)</sup>	-	74.1	89,2	65.5
HEC/10	-	87.4	80.0	12.2
HEC/11 <sup>d)</sup>	-	92.8	91,3	67.9
HEC/12	-	80.4	87,4	33.3
HEC/13	-	73.1	88,9	25.0
SDS	96,0	76,0	-	100
HEC	94,3	78,2	81,5	57.1
HEC/MW	-	81,0	88,6	57.9
CMC	94.6	55,0	70.0	-

SDS – Sodium dodecyl sulphate

(-) – not determined

### 3. CONCLUSION

The partial hydrophobization of HEC was performed by transesterification with MERO and rape seed oil in system H<sub>2</sub>O/DMF at mild reaction conditions under the microwave irradiation and yielded the water – soluble surface - active esters. The microwave irradiation reduced the reaction time of transesterification from several hours to just few minutes. Products were obtained with higher yields as compared to conventional heating. In spite of the very low degrees of substitution achieved, the new synthesized esters of HEC exhibited very positive surface - active and performance properties, such as excellent emulsifying activity, washing power and antiredepositive efficiency. Emulsifying activity for oil/water type emulsion with excellent stability, can be compared to that of the emulsion prepared by the commercial emulsifier Tween 20. Washing power was excellent, too and compared to the sodium dodecyl sulfate as control, even if tested at lower polymer concentration and washing temperature. Antiredepositive activity was higher as exceeding HEC and CMC, which are used as protective colloid as well as lowering surface tension of water. The results substantiate the importance of partially hydrophobized HEC by transesterification with MERO and rape seed oil under microwave assistance as novel polymeric surfactants with potential industrial application.

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